Synthesis of Small Diameter Carbon Nanotubes and Mesoporous Carbon Materials for Hydrogen Storage

-Carried in the "DOE Center of Excellence on Carbon-Based Hydrogen Storage Materials"

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Duke University

05/18/2006

This presentation does not contain any proprietary or confidential information

Project ID # STP19

Overview

Timeline

- Project start date: 2/01/2005
- Project end date: 1/31/2010
- New Start

Budget

- Expected Total Funding
  - DOE share: $500,000
  - Contractor share: $125,000
- Funding for FY05
  - DOE Share: $65,000
  - Contractor share: $25,000
- Funding for FY06
  - DOE Share: $100,000
  - Contractor share: $25,000

Barriers and Targets

- Barriers addressed

  A. Cost.

  B. Weight and Volume.

  C. Efficiency.

  M. Hydrogen Capacity and Reversibility.
- Targets

  Gravimetric capacity: >6%

  Volumetric capacity: >0.045 kg/L

Partners

- Interactions/ collaborations
  - NREL
  - Rice University
  - UNC
  - Oak Ridge

Objectives of Research

- Phase I: (FY05-FY06)
  - Understand the effect of diameters of nanotubes on their hydrogen storage properties;
  - Develop method to precisely control the diameter of the produced nanotubes
  - Understand and demonstrate the effect of metal loading on nanotube on the hydrogen storage properties
  - Synthesis mesoporous carbon materials with high surface area for study in hydrogen storage
  - Study the effect of metal loading on mesoporous carbon on the hydrogen storage properties
  - Goals:
    - Demonstrate small diameter single walled carbon nanotubes have the potential to meet DOE 2010 goal in hydrogen storage properties;
    - Demonstrate the storage potential for mesoporous carbon materials with metal loading to meet/exceed DOE 2010 goal in both Gravimetric and Volumetric capacity.

- Phase II: (FY07-FY09)
  - Demonstration of the large scale production capability for small diameter Single walled carbon nanotubes;
  - Establish capability to prepare high surface area mesoporous carbon materials with right amount of metal loading at 100g/day level for large scale testing
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    - Establish scalable production process for the production of carbon based materials that meet DOE 2010 goal for hydrogen storage.

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Approaches

Control of nanomaterial dimensions is critical to developing high capacity hydrogen storage materials. Both diameters of SWNTs and pore sizes of carbon materials have been shown to affect hydrogen uptake. It is important to develop methods to precisely control these parameters.

Duke is developing novel methods to prepare small diameter and uniform SWNTs by precise control of catalyst diameter and carbon feeding rate.

In addition, Duke is developing novel methods to prepare mesoporous carbon using inorganic/organic templates and advanced chemical vapor deposition techniques. This enables us to prepare mesoporous carbon materials with controlled pore sizes.

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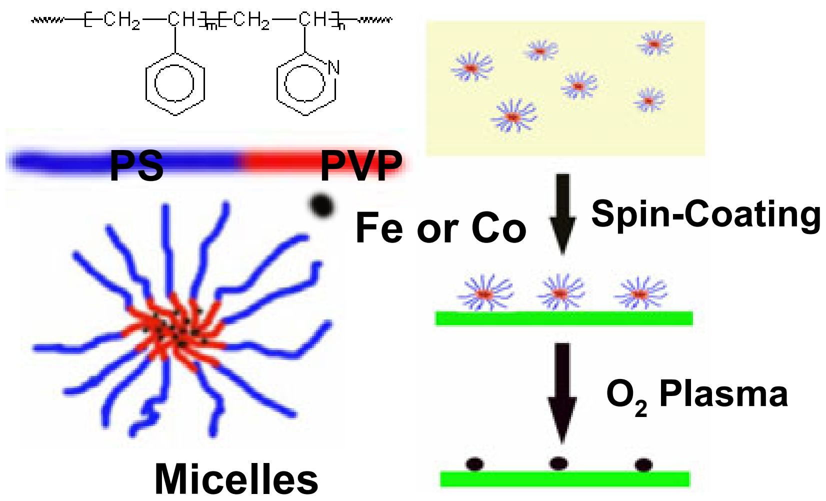
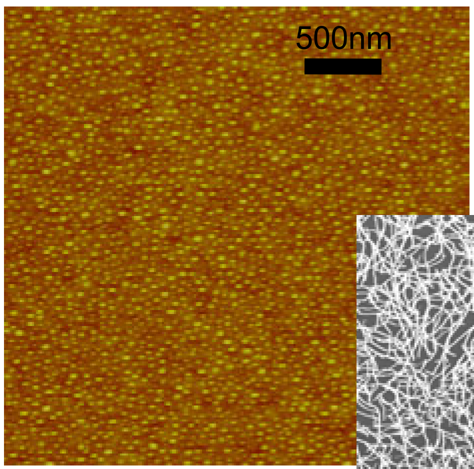
Technical Accomplishments

- Developed method to prepare uniform catalyst nanoparticles for the synthesis of small diameter carbon nanotubes;
- Developed understanding on the relation between the carbon feeding rate and the diameter of prepared nanotubes. Identified conditions under which small diameter CNTs can be prepared;
- Developed three methods to prepare mesoporous carbon materials;
- Developed methods to decorate CNTs and mesoporous carbon materials with small metal nanoparticles for the study of their effect on hydrogen storage properties.

Demonstrated the Control of CNT Diameters through Size Control of Catalysts.

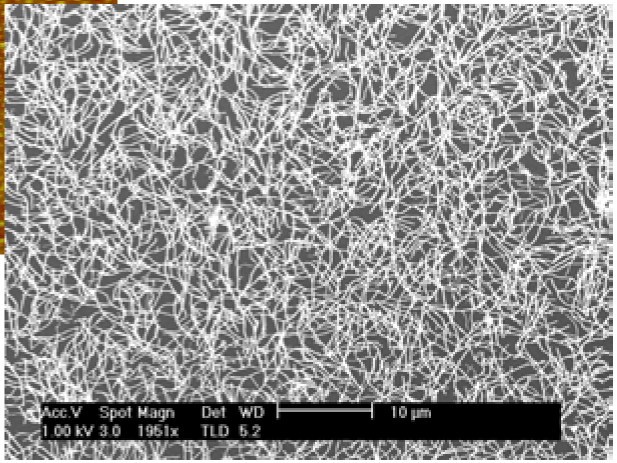
Dicoblock (PS-PVP) copolymer was used to control the size of catalyst nanoparticles. These diblock copolymers can form uniform reversed micelles with the interior decorated by metal ions. After treatment using oxygen plasma, uniform metal oxide nanoparticles can be formed. These uniform metal oxide catalysts can be used to grow uniform CNTs with their diameters controlled by the catalyst size.





AFM image of uniform catalyst nanoparticles

SEM image of uniform small diameter CNTs



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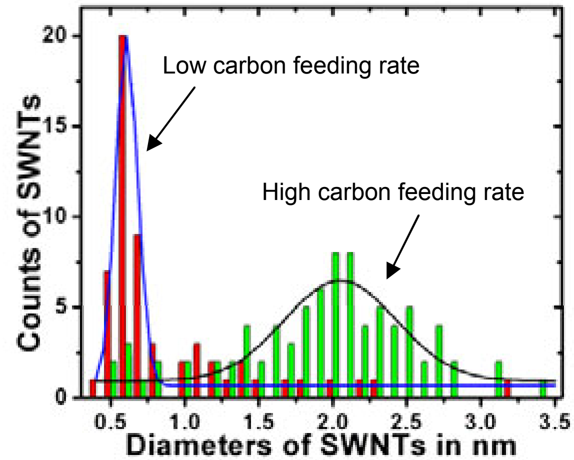

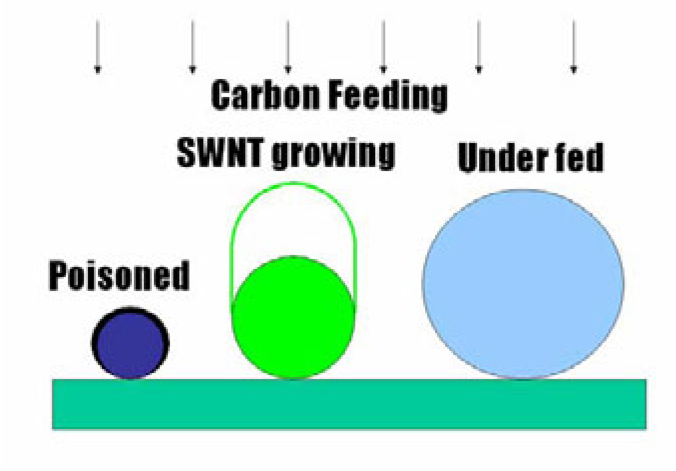

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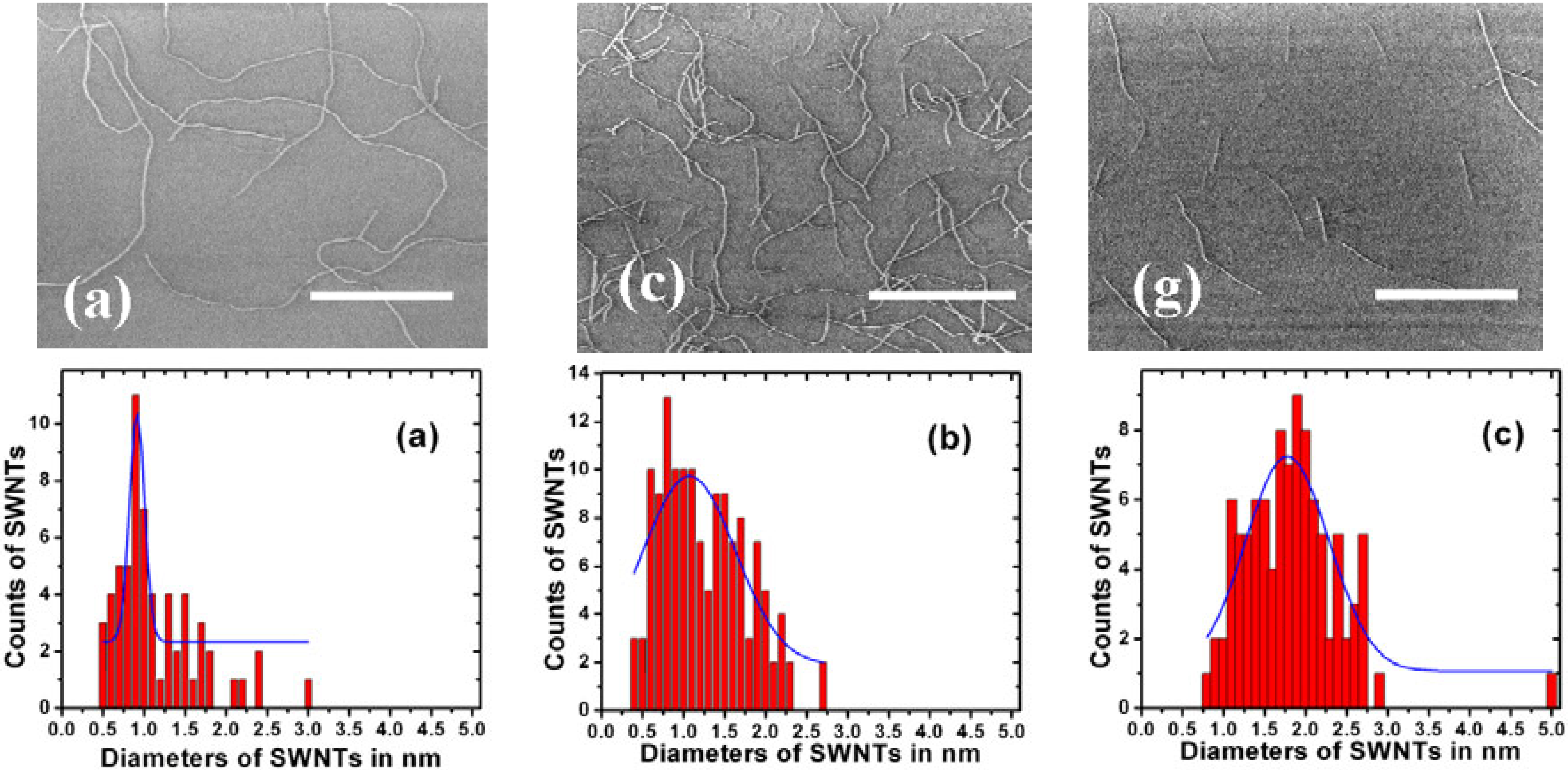

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Prepared High Surface Area Mesoporous Carbon Materials

Motivation:

- High surface area is believed to be a key parameter for high hydrogen storage capacity;
- Controlled pore size is a key for tuning the interaction between the carbon surface and the hydrogen molecules;

Approaches:

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1. Inorganic Template
2. Organic Template
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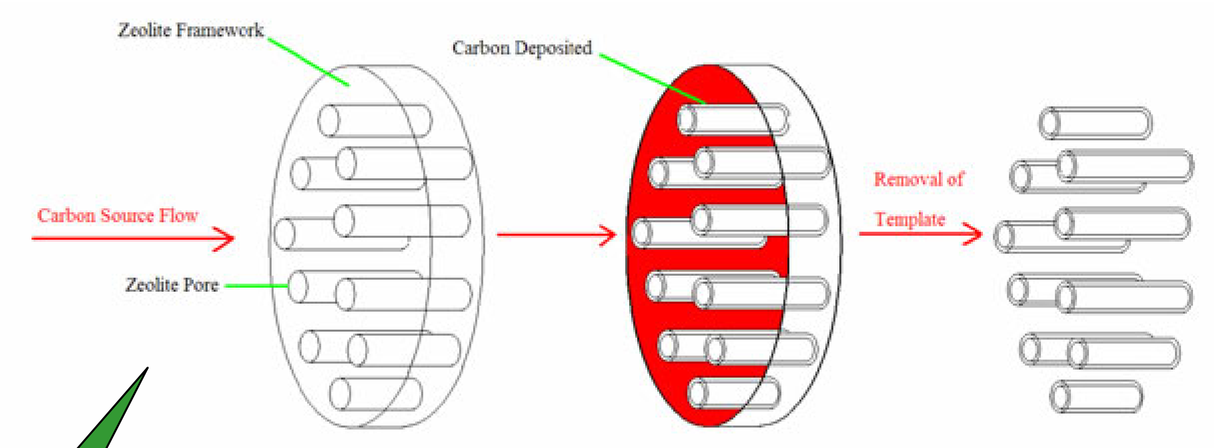
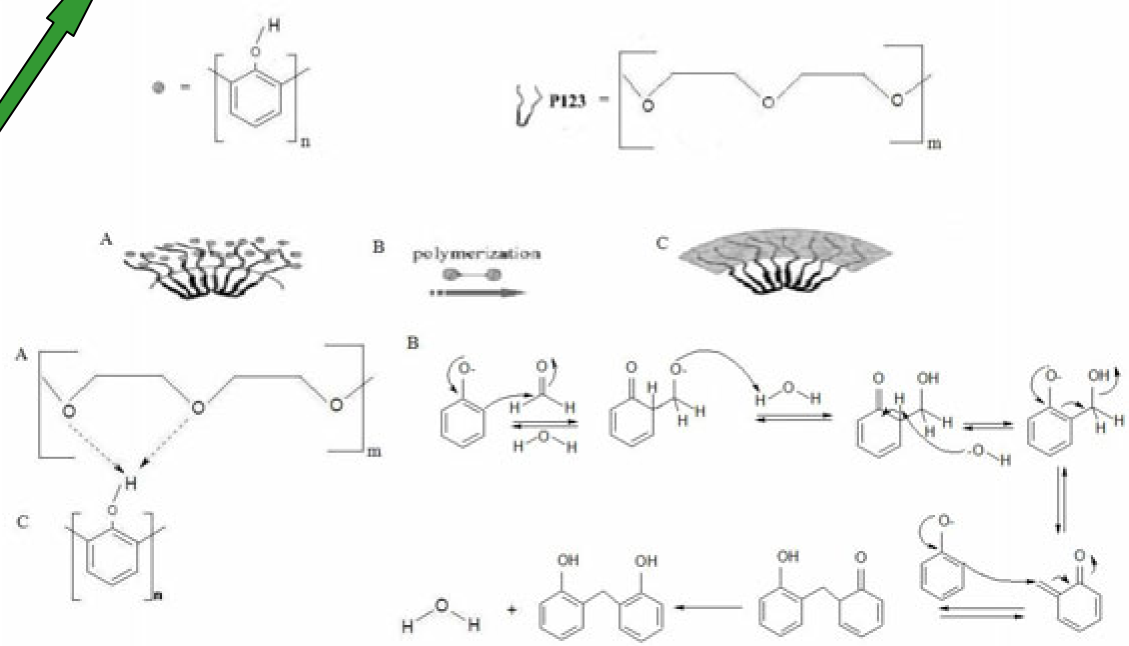
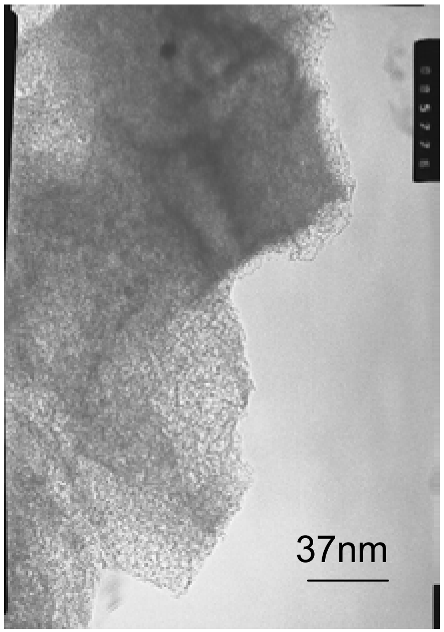
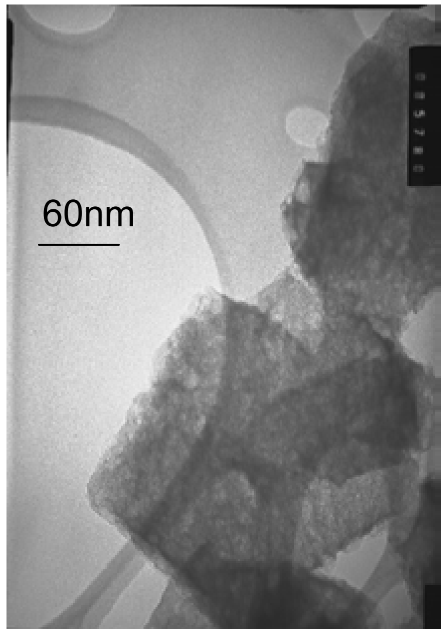
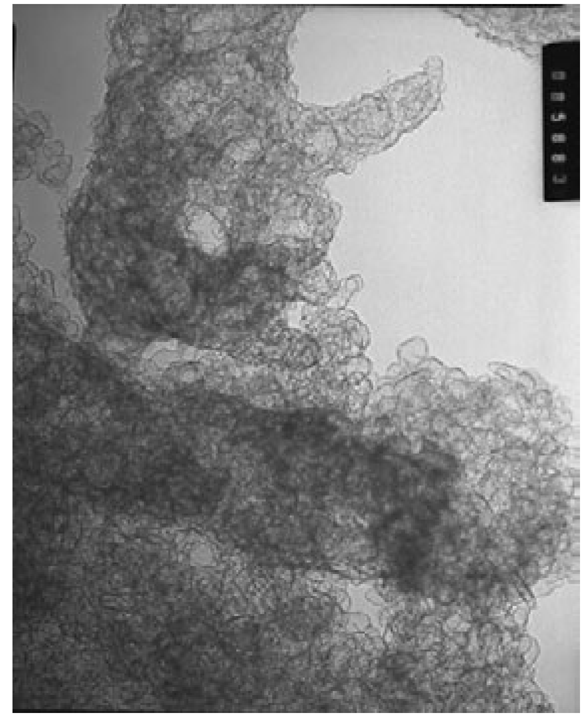




High Surface area Mesoporous Carbon Materials were Prepared using Both Nanocasting and CVD







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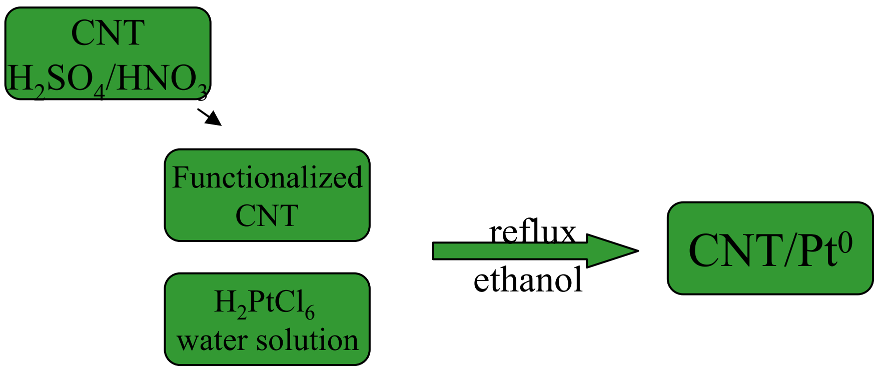

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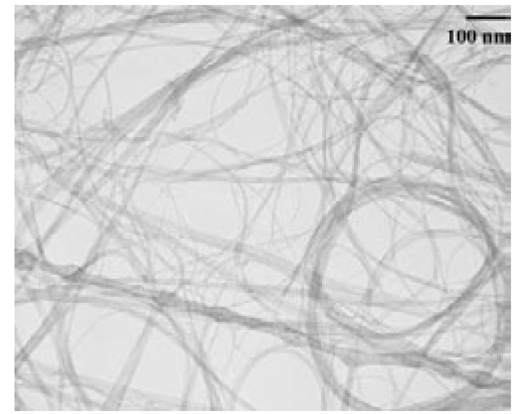

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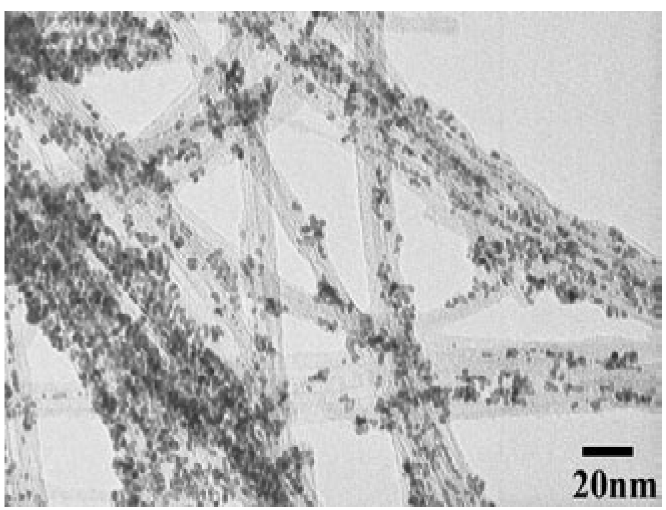
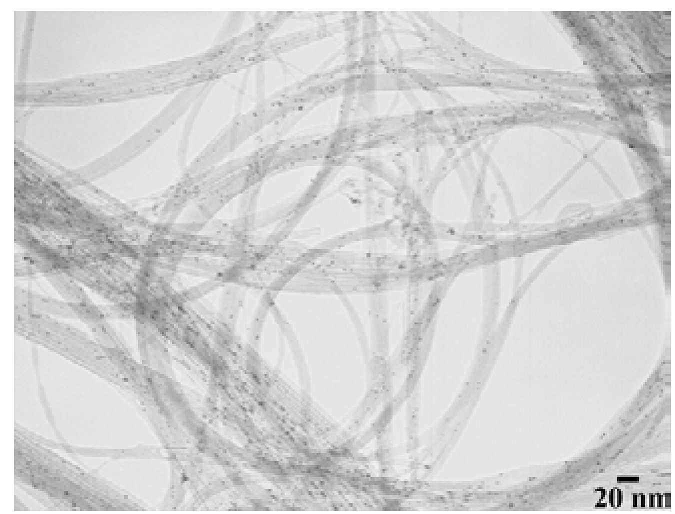


CNT with 70% Pt by weight



CNT with 7% Pt by weight

Measure H_2 Uptake on Pt Decorated CNTs (Data From NREL)

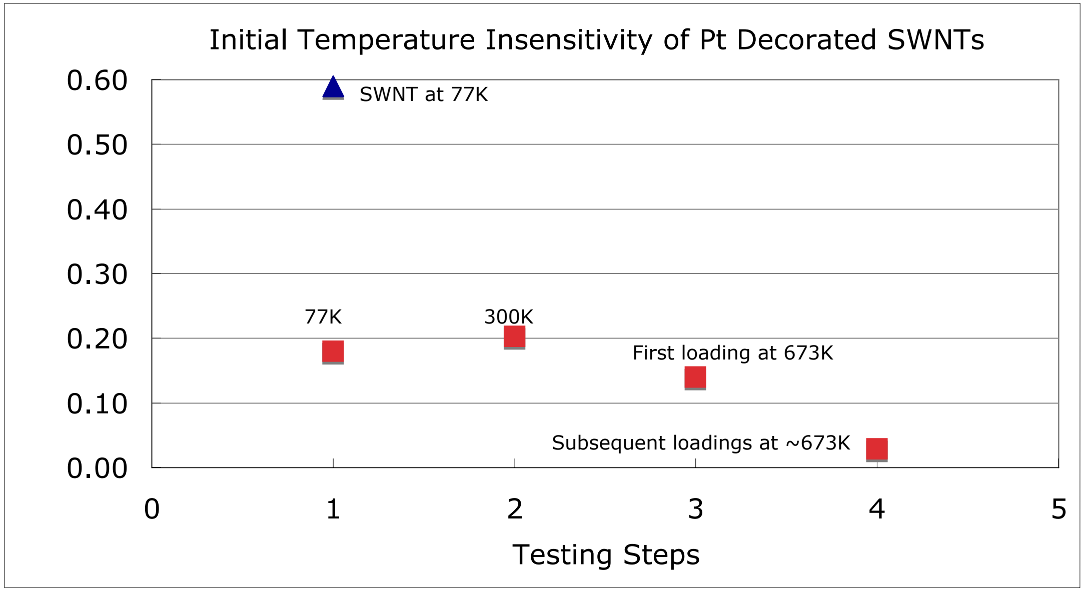
Measurements:

Both Purified CNTs and Pt decorated CNTs were sent to NREL team for hydrogen storage capacity characterization. A similar uptake of hydrogen was observed for Pt decorate CNT samples at room temperature and ~673 K as at low temperature (77 K). This is not expected for a "physisorption" dominated hydrogen sorption mechanism where uptake typically decreases substantially as the temperature increases, indicating a possible "spill-over " effect on the metal decorated CNT samples. More detailed study on metal decoration is on-going.

Storage Capacity:

Purified CNT: 0.6% at 2 bar and 77K

CNT decorated with Pt nanoparticles (70% by weight): 0.2% at both 77K and room temperature.



Measure H2 Uptake of Pt Decorated CNT Samples at ~2 bar Hydrogen Pressure and Different Temperatures.

Small Pt nanoparticles may enable more efficient "spill-over' effect that will lead to higher storage capacity.

Summary Table

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)				
Storage Parameter	**Units**	**2010 System Target**	**FY05 materials****	**FY06 Result**
Specific Energy	kWh/kg (wt. % H2)	2.0 (6 wt.%)	N/A	0.6 wt%*, (2 bar, 77K)
Volumetric Energy Capacity)	kWh/L	1.5		
Desorption Temperature				
Plateau Pressure				

* Measurements were performed at 2 Bar pressure, higher pressure measurement up to 70 bar is scheduled for FY 06-07.

Future Work

- Bulk Synthesis of small diameter SWNTs (FY 06-07):
  - Extend our understanding on the diameter control to bulk synthesis and make gram quantity small diameter nanotubes, Demonstrating that Small diameter CNTs can satisfy DOE 2010 goal for hydrogen storage;
  - Study the diameter effect of hydrogen storage using thin film samples (On-going collaboration with NREL, FY 06)
- Diameter control in mesoporous Carbon Materials (FY 06-07)
  - Preparation of mesoporous carbon materials with controlled pore size and volume. Perform detailed analysis and measurement on the hydrogen storage capability. Demonstrate the material's storage capacity exceeds DOE goal of 6% by weight.
- Study the effect of metal loading on hydrogen storage capacity (FY06)
  - Study the effect of metal decoration on carbon materials on hydrogen storage capacity. Provide more samples with different metal (Pt and Pd) and different loading percentage (1% to 10%) for measurement of storage capacity. Demonstrate the metal decorated carbon materials can be used to meet DOE 2010 requirements.

On-Going and Expected Collaboration

- Rice University
  - “cloning” of nanotubes.
  - Nanotube structural and purity characterization.
- NREL
  - Characterization of nanotubes and mesoporous carbon samples for their structures and hydrogen storage properties.
  - Study the effect of CNT diameter on hydrogen storage properties.
- Oak Ridge
  - Collaboration on nanotube growth and structure characterization

Project Summary

Relevance:

- Help to understand fundamental questions related to hydrogen storage in carbon materials.

Approach:

- Controlling the diameter of SWNTs;
- Controlling the pore size and volume of mesoporous carbon materials using templates.
- Attach small metal nanoparticles on carbon materials to improve storage capacity.

Technical Accomplishments:

- Discovered a catalyst preparation method that is suitable for the preparation of small diameter CNTs;
- Discovered the relation between the carbon feeding rate and the diameter of prepared nanotubes;
- Prepared mesoporous carbon materials using three different methods;
- Prepared metal decorated CNTs and mesoporous carbon materials and delivered to other center members for measurements.

Proposed Future research:

- Bulk Synthesis of small diameter SWNTs;
- Diameter control in mesoporous Carbon Materials;
- Study the effect of metal loading on hydrogen storage capacity.

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j.liu@duke.edu

Publications

1. “Relation Between the Yield, the Diameter of Single Walled Carbon Nanotubes and the Growth Conditions in a Chemical Vapor Deposition Process”, Chenguang Lu, Jie Liu, Submitted to **Nano Letters** (2006).
2. “Growth of Uniform Small Diameter Single Walled Carbon Nanotubes using Co as Catalysts”, Dongning Yuan, Qiang Fu, Jennifer Lu and Jie Liu. **In preparation.** (2006)

Critical Assumptions and Issues

Critical Assumptions:

1. Small diameter SWNTs (< 1nm) will have higher hydrogen storage capacity than SWNTs with larger diameter. Supported by theoretical calculation from Air Product:

   Cheng, H., Pez, G. P., and Cooper, A. C. Mechanism of hydrogen sorption in single-walled carbon nanotubes. Journal of the American Chemical Society, *123:* 5845-5846, 2001.

   Kostov, M. K., Cheng, H., Cooper, A. C., and Pez, G. P. Influence of carbon curvature on molecular adsorptions in carbon-based materials: A force field approach. Physical Review Letters, *89*, 2002.

2. Metal Decoration on CNTs and other carbon materials can improve hydrogen storage at higher temperature. Supported by initial data from NREL on Pt decorated CNTs and work from the CoE team member at University Michigan, Ralph Yang's group.

   Yang, F. H., Lachawiec, A. J., and Yang, R. T. Adsorption of spillover hydrogen atoms on single-wall carbon nanotubes. Journal of Physical Chemistry B, *110:* 6236-6244, 2006.

   Lachawiec, A. J., Qi, G. S., and Yang, R. T. Hydrogen storage in nanostructured carbons by spillover: Bridge-building enhancement. Langmuir, *21:* 11418-11424, 2005.

3. High Surface area mesoporous carbon materials may be a good candidate for hydrogen storage.

   These materials have similar structure as short segments of nanotubes. If the pore size can be controlled to the same dimension as SWNTs, they can provide as good a media for hydrogen storage as CNTs.

Critical Assumptions and Issues

Remaining Issues:

1. How to control the diameter of SWNTs and make SWNTs in large scale and with low cost?
   - Cost of nanotube is too high now and it will eventually be an issue. CVD is the best approach to solve the problem but more work is needed in controlling the diameter of nanotubes in large scale synthesis.
2. Is SWNT the best carbon material for hydrogen storage or other forms of carbons, like mesoporous carbon, are as good?
   - If mesoporous carbon or other form of carbon with high surface area can offer as good or better storage capacity than SWNTs, it will provide a more economical solution for hydrogen storage in carbon based materials. So it is worthwhile to look into it carefully.
3. What is the mechanism for enhancing the hydrogen storage capacity through metal decoration? What metal is best suited for the application? These questions need to be addressed through research in the near future.

Approaches

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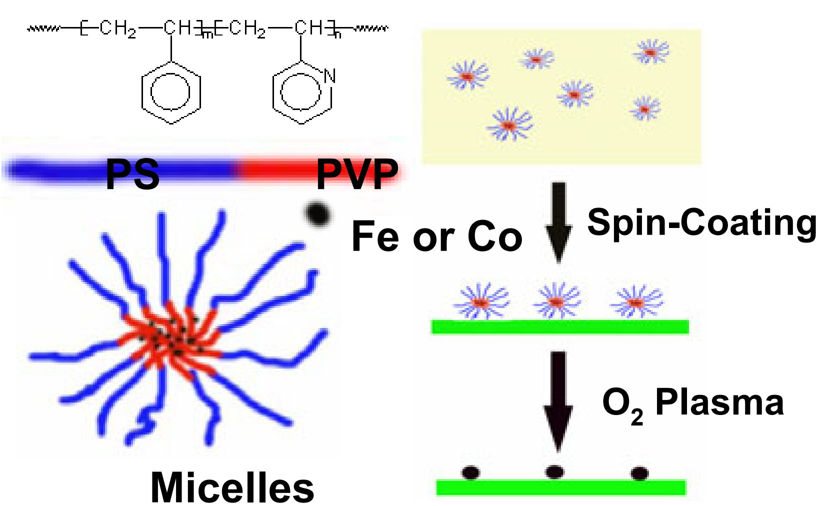

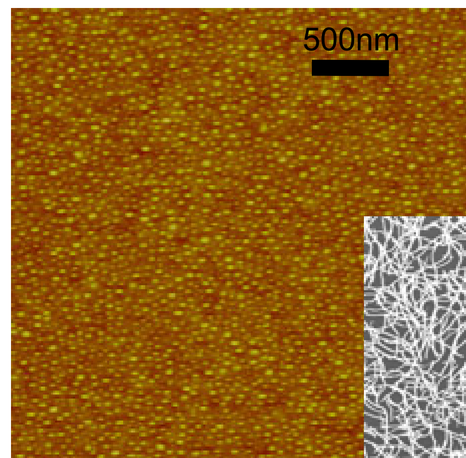

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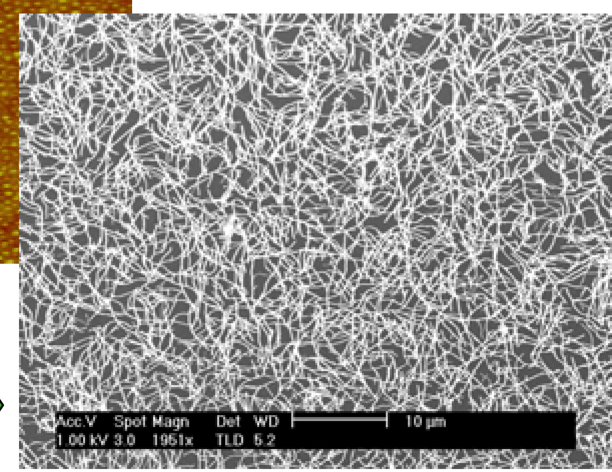

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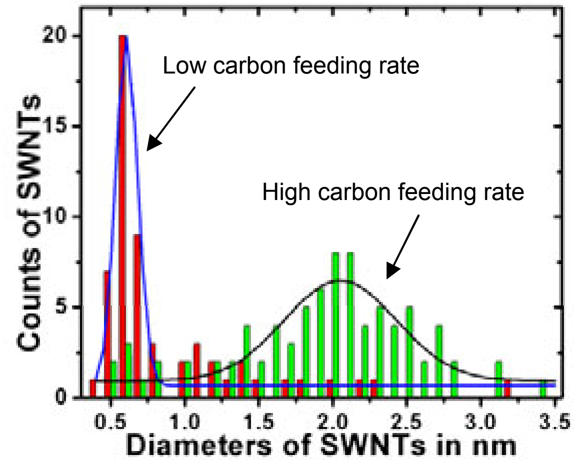

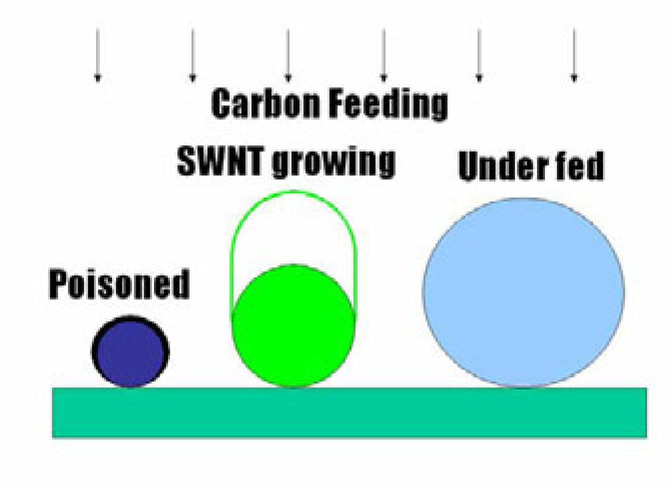

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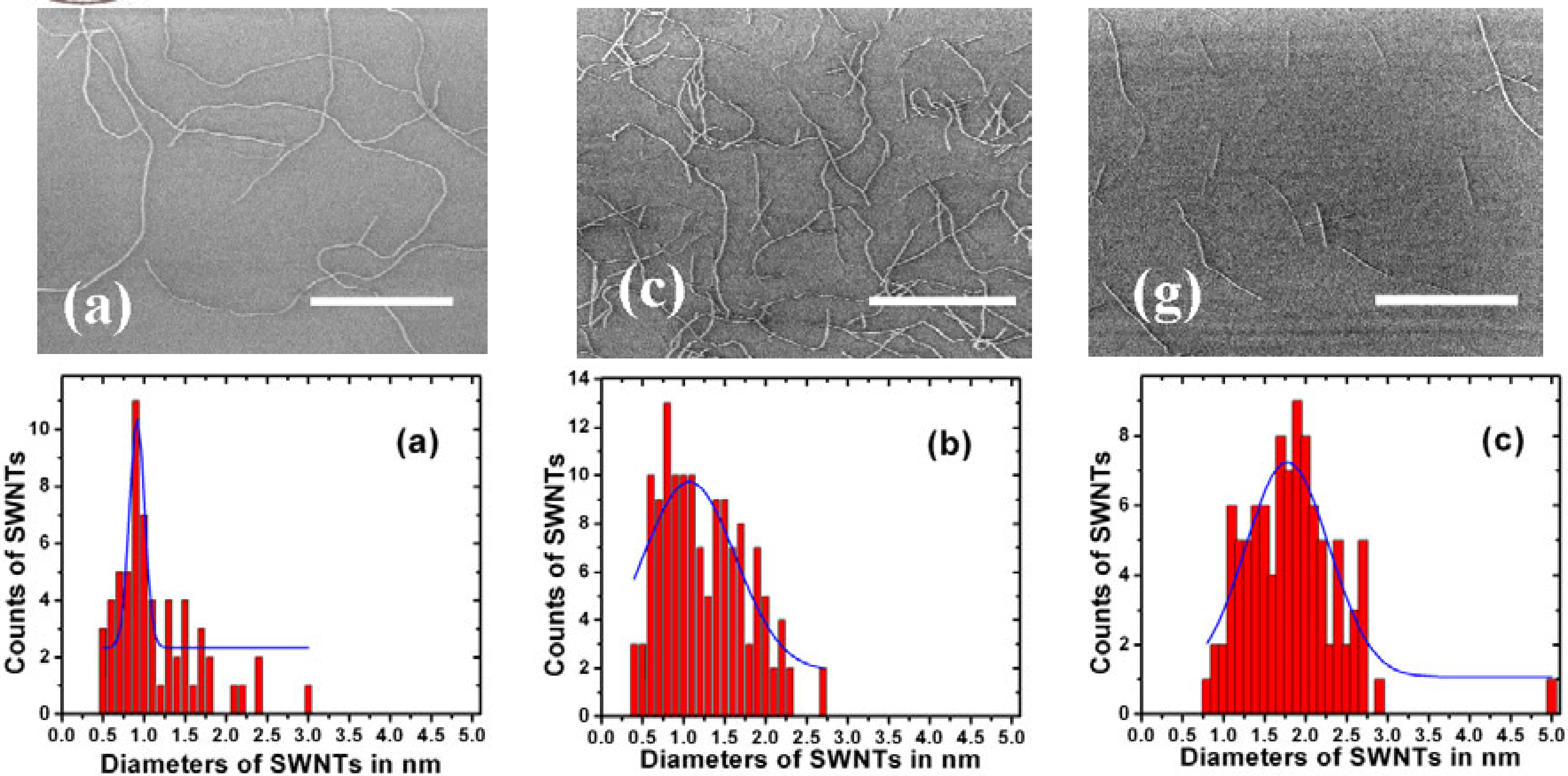

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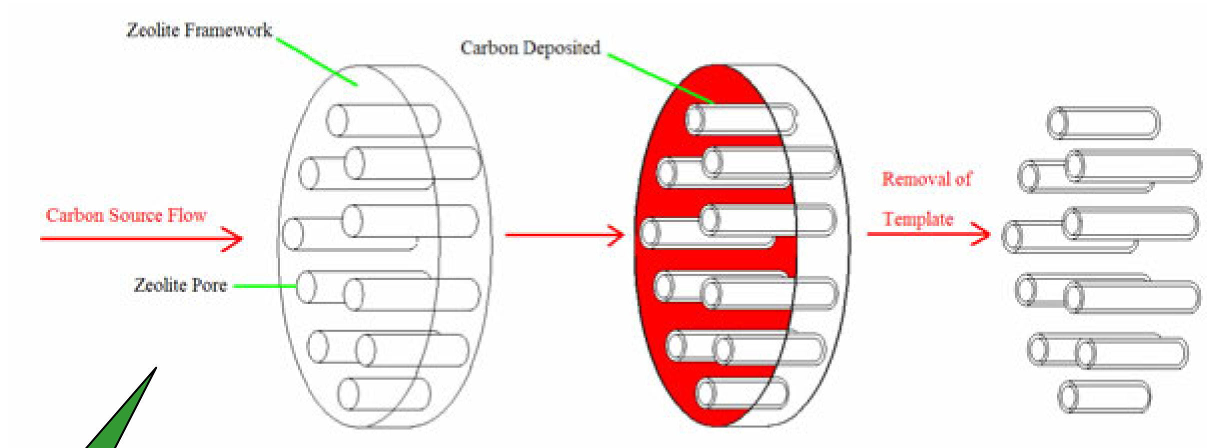

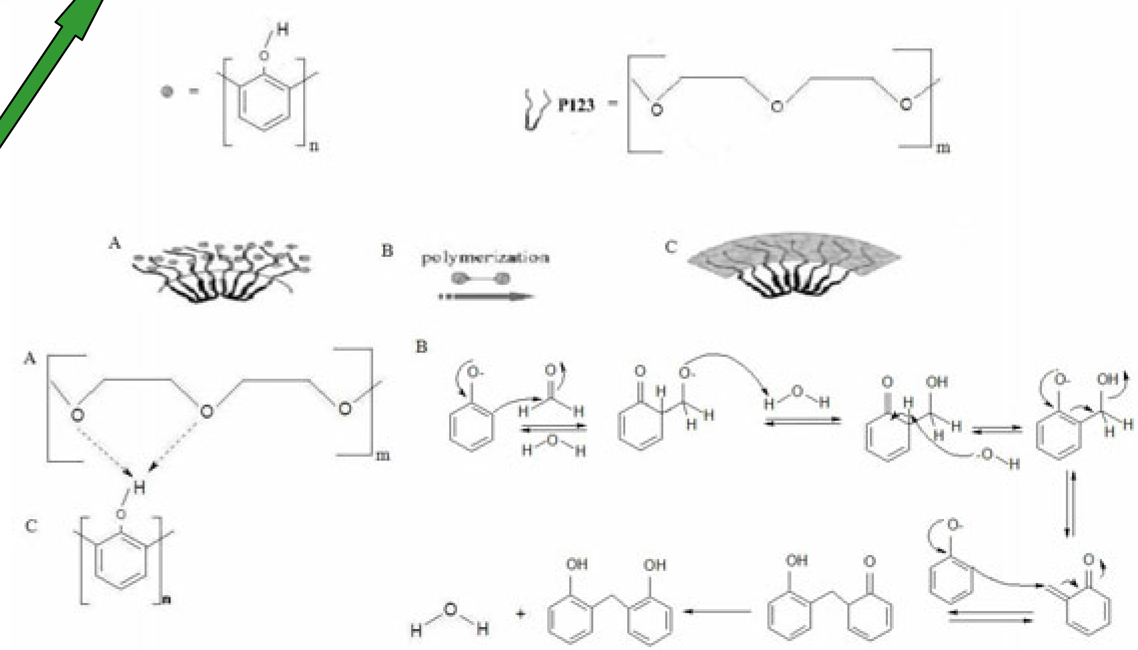

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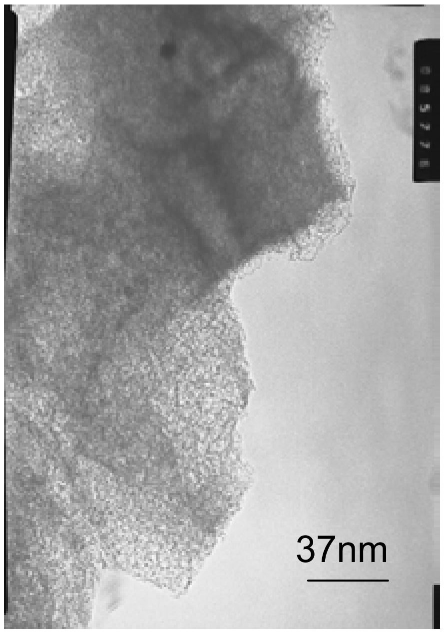

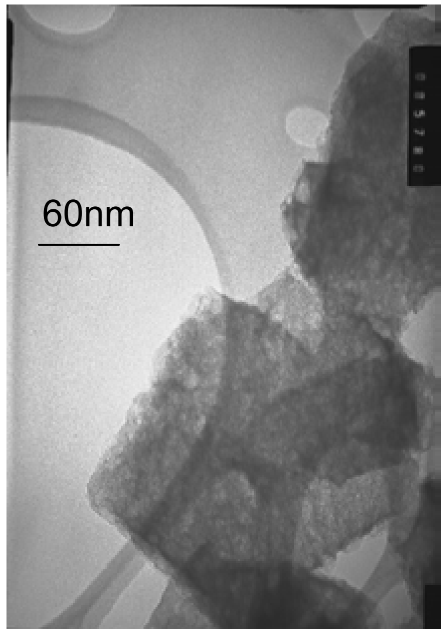

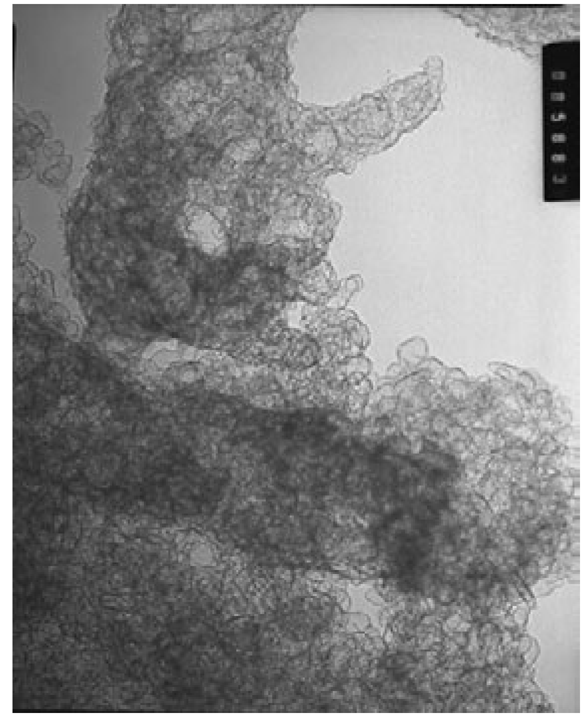

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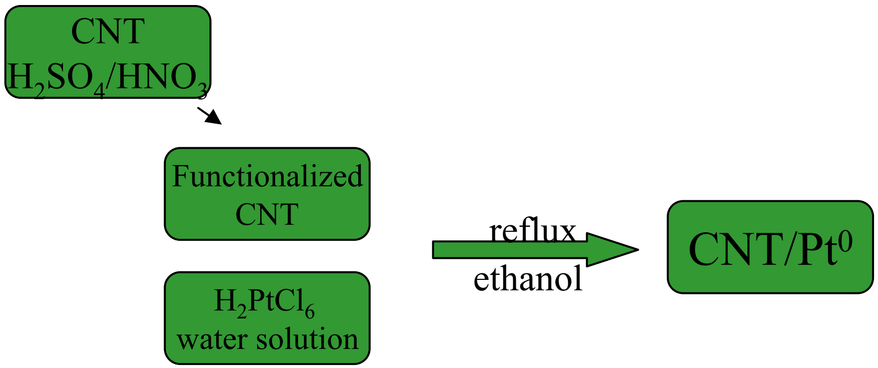

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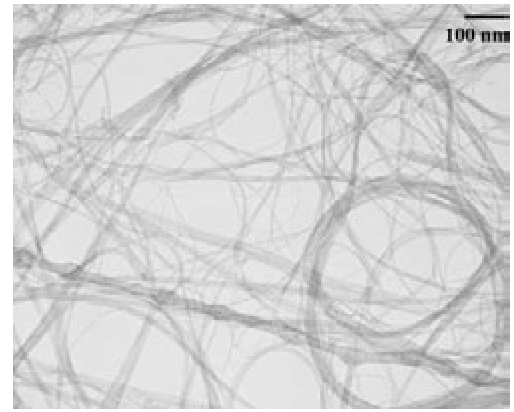

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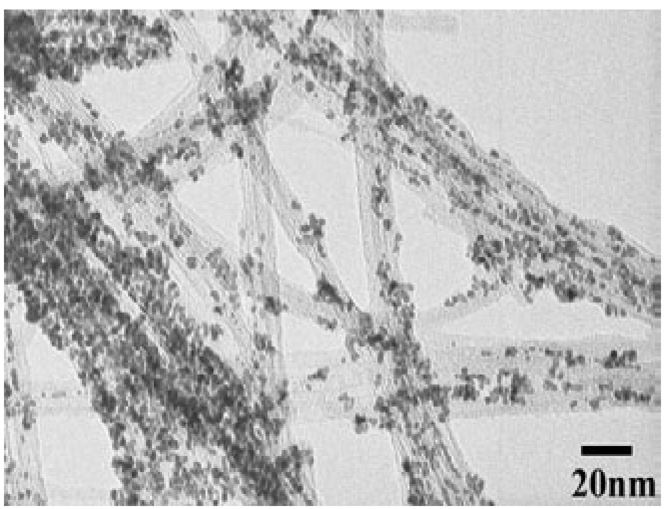

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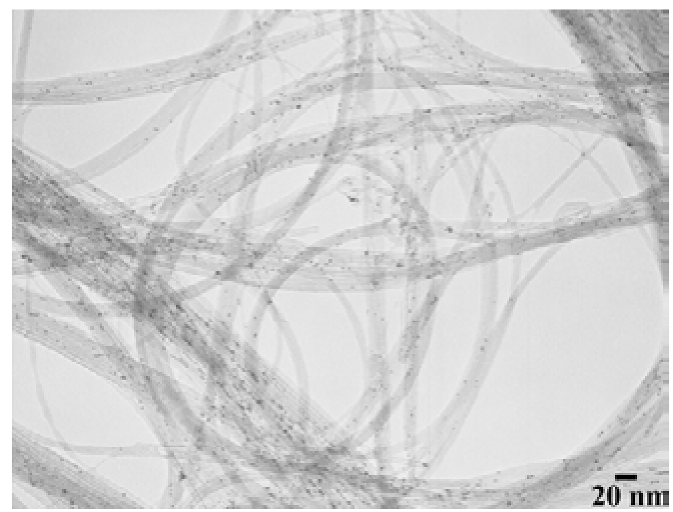

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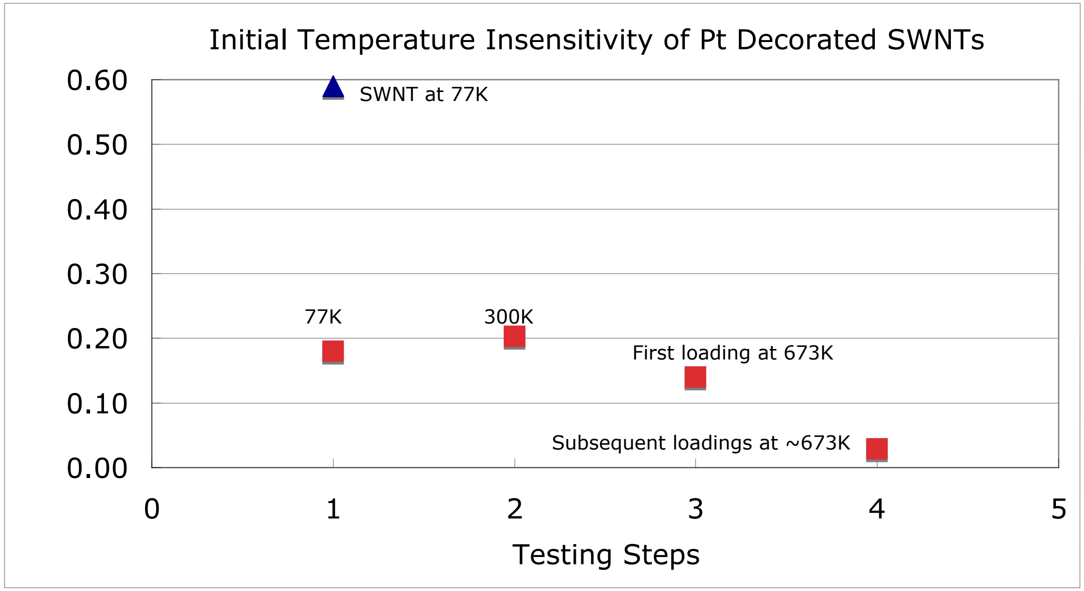

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Future Work

- Bulk Synthesis of small diameter SWNTs (FY 06-07):
  - Extend our understanding on the diameter control to bulk synthesis and make gram quantity small diameter nanotubes, Demonstrating that Small diameter CNTs can satisfy DOE 2010 goal for hydrogen storage;
  - Study the diameter effect of hydrogen storage using thin film samples (On-going collaboration with NREL, FY 06)
- Diameter control in mesoporous Carbon Materials (FY 06-07)
  - Preparation of mesoporous carbon materials with controlled pore size and volume. Perform detailed analysis and measurement on the hydrogen storage capability. Demonstrate the material's storage capacity exceeds DOE goal of 6% by weight.
- Study the effect of metal loading on hydrogen storage capacity (FY06)
  - Study the effect of metal decoration on carbon materials on hydrogen storage capacity. Provide more samples with different metal (Pt and Pd) and different loading percentage (1% to 10%) for measurement of storage capacity. Demonstrate the metal decorated carbon materials can be used to meet DOE 2010 requirements.

On-Going and Expected Collaboration

- Rice University
  - “cloning” of nanotubes.
  - Nanotube structural and purity characterization.
- NREL
  - Characterization of nanotubes and mesoporous carbon samples for their structures and hydrogen storage properties.
  - Study the effect of CNT diameter on hydrogen storage properties.
- Oak Ridge
  - Collaboration on nanotube growth and structure characterization

Project Summary

Relevance:

- Help to understand fundamental questions related to hydrogen storage in carbon materials.

Approach:

- Controlling the diameter of SWNTs;
- Controlling the pore size and volume of mesoporous carbon materials using templates.
- Attach small metal nanoparticles on carbon materials to improve storage capacity.

Technical Accomplishments:

- Discovered a catalyst preparation method that is suitable for the preparation of small diameter CNTs;
- Discovered the relation between the carbon feeding rate and the diameter of prepared nanotubes;
- Prepared mesoporous carbon materials using three different methods;
- Prepared metal decorated CNTs and mesoporous carbon materials and delivered to other center members for measurements.

Proposed Future research:

- Bulk Synthesis of small diameter SWNTs;
- Diameter control in mesoporous Carbon Materials;
- Study the effect of metal loading on hydrogen storage capacity.

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Publications

1. "Relation Between the Yield, the Diameter of Single Walled Carbon Nanotubes and the Growth Conditions in a Chemical Vapor Deposition Process", Chenguang Lu, Jie Liu, Submitted to **Nano Letters** (2006).
2. "Growth of Uniform Small Diameter Single Walled Carbon Nanotubes using Co as Catalysts", Dongning Yuan, Qiang Fu, Jennifer Lu and Jie Liu. **In preparation.** (2006)

Critical Assumptions and Issues

Critical Assumptions:

1. Small diameter SWNTs (< 1nm) will have higher hydrogen storage capacity than SWNTs with larger diameter. Supported by theoretical calculation from Air Product:

   Cheng, H., Pez, G. P., and Cooper, A. C. Mechanism of hydrogen sorption in single-walled carbon nanotubes. Journal of the American Chemical Society, *123:* 5845-5846, 2001.

   Kostov, M. K., Cheng, H., Cooper, A. C., and Pez, G. P. Influence of carbon curvature on molecular adsorptions in carbon-based materials: A force field approach. Physical Review Letters, *89*, 2002.

2. Metal Decoration on CNTs and other carbon materials can improve hydrogen storage at higher temperature. Supported by initial data from NREL on Pt decorated CNTs and work from the CoE team member at University Michigan, Ralph Yang's group.

   Yang, F. H., Lachawiec, A. J., and Yang, R. T. Adsorption of spillover hydrogen atoms on single-wall carbon nanotubes. Journal of Physical Chemistry B, *110:* 6236-6244, 2006.

   Lachawiec, A. J., Qi, G. S., and Yang, R. T. Hydrogen storage in nanostructured carbons by spillover: Bridge-building enhancement. Langmuir, *21:* 11418-11424, 2005.

3. High Surface area mesoporous carbon materials may be a good candidate for hydrogen storage.

   These materials have similar structure as short segments of nanotubes. If the pore size can be controlled to the same dimension as SWNTs, they can provide as good a media for hydrogen storage as CNTs.

Critical Assumptions and Issues

Remaining Issues:

1. How to control the diameter of SWNTs and make SWNTs in large scale and with low cost?
   - Cost of nanotube is too high now and it will eventually be an issue. CVD is the best approach to solve the problem but more work is needed in controlling the diameter of nanotubes in large scale synthesis.
2. Is SWNT the best carbon material for hydrogen storage or other forms of carbons, like mesoporous carbon, are as good?
   - If mesoporous carbon or other form of carbon with high surface area can offer as good or better storage capacity than SWNTs, it will provide a more economical solution for hydrogen storage in carbon based materials. So it is worthwhile to look into it carefully.
3. What is the mechanism for enhancing the hydrogen storage capacity through metal decoration? What metal is best suited for the application? These questions need to be addressed through research in the near future.